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GAS-DYNAMIC MODEL OF THE FORMATION OF OPEN AND CLOSED POROSITY IN SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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A gas-dynamic model of the formation of open and closed porosity of materials under the conditions of combustion in SHS systems, when a liquid phase (which can boil under certain conditions), impurity-gas pressure, vapor-phase pressure, and external pressure or vacuum exist, is examined. It is shown that there exists a critical pressure which characterizes the boundary of the transition of closed to open porosity. Experimental studies for the system Ti – C showed that the size of the open pores of a synthesized sample, measured according to the volume of the sample, correlates with the computed values obtained in a study of the gas-dynamic model of the formation of open porosity using the theory of cavitation.

Key words: open and closed porosity of materials, microstructure, temperature, combustion, method of self-propagating high-temperature synthesis (SHS).

The basic concept of the gas-dynamic model of the formation of open porosity and closed porosity in self-propagating high-temperature synthesis (SHS) reduces to the following. At time $t = 0$ the batch metal melts in a combustion wave (SHS process) and undergoes capillary flow with formation of a liquid interlayer (phase). As a number of authors assert, the formation of open porosity occurs mainly as the impurity gases released in the SHS process filtrate through the liquid phase of the synthesized product [1 – 5]. However, in the published works examining the model of the formation of open and closed porosity the pressure of the surrounding medium within wide limits (including vacuum) and the pressure of the liquid phase of the SHS system, which could reach tens of atmospheres, were neglected [6, 7]. The conditions where the closed porosity of the synthesized materials can transform into open porosity likewise were not studied. It should be noted that the pressure of the surrounding medium strongly affects the boiling temperature of the initial products of synthesis. For example, the boiling temperature of cobalt at the argon pressure 1 atm (1 atm = 10^5 Pa) is 3100°C, while at $p = 0.1$ mm Hg (10 Pa) it is only 1645°C [6]. It can be assumed that in many cases of SHS processes in vacuum the

charge metals not only melt but also boil. Strictly speaking, the melting temperature of the materials also depends on the external pressure, and it can be calculated using the well known empirical Antoine equation

$$\log p = A - B/(T + C),$$

where A , B , and C are empirical individual constants [6].

For this reason it is natural that a correction must be introduced at low and high pressures of the surrounding medium in phase diagram of some systems which was obtained under standard conditions.

Thus, at the formulation level the present authors adopted the following initial conditions with citations to the literature: the combustion temperature of the SHS system; a liquid phase which can boil under certain conditions; the pressure due to the impurity gases, the liquid-phase vapors, and the external atmosphere (including a vacuum). Porosity forms in the sample under such conditions. The authors do not examine in the proposed model the equations of chemical kinetics and heat balance in a coordinate system tied to the moving combustion front, which likewise is not used in some of the citations presented.

In the present article a gas-dynamic model of the formation of open and closed porosity under the initial conditions adopted and using the theory of cavitation is presented [8].

The theory of cavitation in this case reduces to the following. If the vapor pressure of the liquid and impurity gases

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in it exceed the external pressure, then very small free bubbles, from which cavitation develops, are formed in the liquid [8]. Any bubble strives to grow at a high rate, depending on the inertia of the surrounding liquid. This growth will occur as a result of the release of impurity gases and evaporation of the liquid from the walls of a bubble (formation of a cavity). For this reason a number of authors call the phenomenon described “vapor cavitation” [8]. Incidentally, water vapor is the main content of a bubble in boiling water.

Let us consider a specific bubble with variable radius in a liquid which is moving radially relative to its center. Strictly, the radial motion is irrotational and described by the velocity potential

$$\varphi = \frac{R^2}{r} \frac{dR}{dt},$$

where $R = R(t)$ is the radius of the bubble; r is the radial distance from the center to the bubble; and, t is the time. In general R and r are not the same.

Then the radial component of the velocity of the liquid relative to the center of the bubble can be represented by the expression

$$U = -\frac{\partial \varphi}{\partial r} = \frac{R^2}{r^2} \frac{dR}{dt}.$$

For constant density and no force of gravity the equation of motion of the liquid has the form

$$-\frac{d\varphi}{dt} + \frac{U^2}{2} + \frac{p}{\rho} = f(t) = p^\infty/\rho,$$

where p^∞ is the pressure in the liquid with $U = 0$ and $\varphi = 0$.

Setting $r = R$ we obtained the equation of motion of the wall of the bubble

$$R \frac{dU}{dt} - \frac{3}{2} U^2 = p^\infty - p/\rho, \quad (1)$$

where $p = p(t)$ is the pressure in the liquid at the wall of the bubble.

Let the bubble be filled with gas and vapor. Then for a perfect gas and vapor pressure at the bubble wall we shall have

$$p = p_v - 2\sigma/R + NT/R^3, \quad (2)$$

where $p_v = p_v(T)$ is the saturated vapor pressure, which can be evaluated from the Clausius – Clapeyron equation

$$\ln p = A - B/T,$$

where $A = \Delta H_w/(RT_w)$; $B = \Delta H_w/R$; ΔH_w is the heat of evaporation; T is the temperature; $\sigma(T)$ is the surface tension; N is a constant for fixed mass of a given gas.

Substituting the expressions (1) in Eq. (2) we obtain

$$\rho \left(R \frac{dU}{dt} - \frac{3}{2} U^2 \right) = -(p^\infty - p + 2\sigma/R - NT/R^3) = f(R, T).$$

If the bubble is in a state of equilibrium, then its critical radius is determined by the expression $f(R, T) = 0$, i.e., R_{cr} is the critical radius determined from the condition $\partial f / \partial R = 0$.

Solving the equation at constant temperature we determine the critical radius as

$$R_{cr} = -4\sigma/(p^\infty - p), \quad (3)$$

where $(p^\infty - p) = p_{cr}$ is the critical pressure.

Thus, performing the mathematical calculations in the proposed gas-dynamic model of the formation of open porosity in SHS processes using cavitation theory at equilibrium we obtain the dependence of the critical radius of a bubble on the critical pressure.

In the case under study, at equilibrium the critical pressure p_{cr} equals the difference of the static pressure of the liquid p^∞ (the pressure in the experimental chamber), the pressure p_g (of the dissolved impurity gas released in the SHS process), and the saturated vapor pressure of the liquid p_v ($p_{cr} = p^\infty - p_g - p_v$). We note that at constant density and irrotational motion the terms in the equation which take account of the viscosity become meaningless.

It should be noted that Eq. (3) is similar to the Laplace equation for the model of the diameter of cylindrical pores [9]

$$D = -4\sigma \cos \theta / p_{cap},$$

where p_{cap} is the capillary pressure; σ is the surface tension of the liquid; and, θ is the wetting angle.

It is well known that the rate of appearance of bubbles depends on the degree of overheating of the liquid and can result in a much more intense process than ordinary boiling — bumping [8]. This gives rise to uncontrollable growth of bubbles, occurring in SHS processes, and spraying of the liquid phase.

Thus, the model studied here can be used to evaluate mathematically the size of the pores in SHS materials and therefore regulate the porosity of the synthesized SHS materials.

As an example, we substituted into the formula the typical parameters for the combustion of the system (Ti – C) to evaluate the permeability and the size of the pores of the synthesized materials: $T_g = 3280$ K, surface tension of titanium $\sigma = 10^3$ dynes/cm (1 N/m), pressure of the liquid in the experimental chamber $p^\infty = 0.1$ mm Hg (10 Pa), and the experimentally measured average pressure of the impurity gases in the combustion front for the system (Ti – C) $p_{com} = 6$ atm (6×10^5 Pa) [5], the vapor pressure of the liquid for titanium $p_v = 1.24$ atm (1.24×10^5 Pa) [6, 7]. As a result of the calculation the critical size of the pores was found to be $21.4 \mu\text{m}$ and the filtration coefficient $2.59 \mu\text{m}^2$.

The synthesis of SHS material with open porosity was also studied experimentally for the system Ti – C. Since the main factor for SHS filters is the presence of through pores (i.e. absence of closed porosity), the authors considered is desirable to synthesize porous material not by means layer-

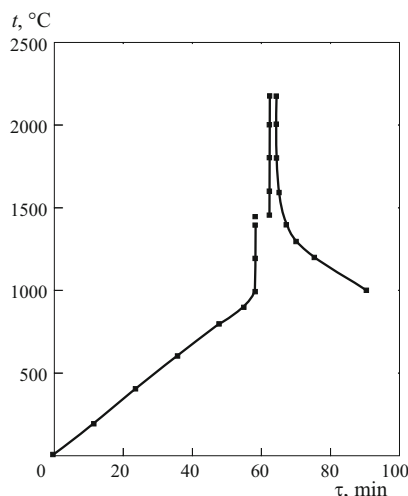


Fig. 1. Variation of the temperature of the charge in the synthesis regime of the samples (Ti – C).

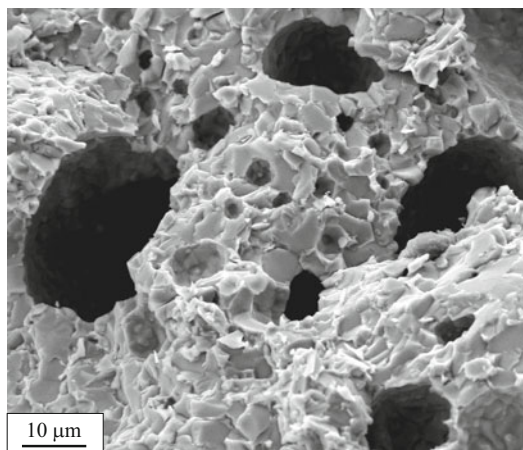


Fig. 2. Microstructure of the synthesized sample from Ti – C.

wise combustion but rather in the thermal explosion regime (in the interior volume of the sample). Ti powder (PTOM grade) with average particle size 5 – 10 μm and graphite with particle size 15 – 20 μm in stoichiometric ratio were used in the system Ti – C in these studies. The powders were mixed for 1 h in a ball mill using Al₂O₃ balls. The ready charge was poured into a graphite mold, which was placed into a vacuum furnace. The temperature of the charge was increased to the self-combustion temperature, after which spontaneous combustion of the charge occurred. Figure 1 shows such a regime for the system Ti – C. The microstructure of the synthesized porous sample is shown in Fig. 2. It should be noted that Fig. 2 shows the morphology of the fracture of the sample obtained, where the dark spots indicate depressions and the roughness of the fracture surface, unevenness, and remains of closed pores. The size of the open pores is the equivalent hydraulic diameter of the channel along which the fluid (gas or liquid), as measured according to GOST 13523–78, flows.

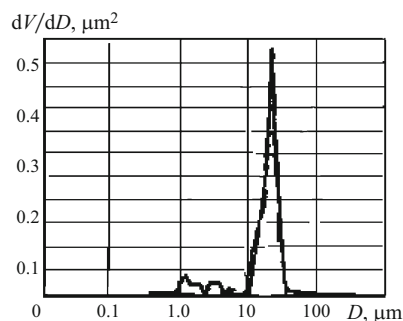


Fig. 3. Differential distribution function of pores over a sample of a ceramic filter element with a uniform structure from Ti – C [average size of the pores — 16.73 μm according to the volume, 15.4 μm according to the surface; average pore size ($4V/A$) — 16.2 μm].

The pore distribution over a sample from Ti – C (Fig. 3) showed that the size of the open pores of a synthesized sample, measured according to the volume of the sample, correlates with the computed values which were obtained in the study of the gas-dynamic model of the formation of open and closed porosity using the theory of cavitation for the conditions of SVS processes (high synthesis temperatures, pressure of the surrounding medium) taking account of the release of impurity gas and the vapor pressure of the liquid phase of the SVS system.

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